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(54) **Filamentary yarn and film of an aromatic polyetherketone**

(57) A process of melt spinning a yarn or of extruding a film from an aromatic polyetherketone in which prior to spinning or extruding, there is admixed with the polyetherketone polymer in excess of 2% by weight of a plasticiser which is thermally stable at the temperature of the melt and provides a melt of reduced viscosity such plasticiser having volatility characteristics such that though some of the plasticiser volatilises from the spun yarn or extruded film during the process, more than 1% by weight of the plasticiser remains in the spun yarn or extruded film.

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SPECIFICATION

Filamentary yarn and film of an aromatic polyetherketone

- 5 This invention relates to the melt spinning of mono- and multi-filament yarns and to the extrusion of a film from an aromatic polyetherketone and more particularly an aromatic polyetheretherketone. 5

We have found it possible to produce extruded products, more particularly melt spun textile filaments, of an aromatic polyetherketone and more particularly an aromatic polyetheretherketone by conventional melt spinning techniques. This involves melting either a powder or granules of the polymer at between 350°C and 400°C and, using a metering screw or pump, passing the melt to a filter pack where the melt is filtered through graded sand, graded gauzes or sintered metal having a pore size down to about 25 microns. The molten polymer is then extruded through a spinneret at 370°C to 400°C into filaments which are drawn down in a controlled cooling environment. Subsequent processing may involve a reheating of the filaments above 150°C and the drawing of the filaments by a factor of about 3 to complete orientation of the filaments. Film can be produced in a similar manner using a slot die rather than a spinneret. 10 15

However with such techniques we have found it becomes increasingly difficult to produce filaments below 100 microns and more particularly below 50 microns. In the production of filaments 'raining' from the spinneret occurs causing very short lengths of increased diameter to occur in the spun filaments at draw down and it is suspected that the breaks which occur both in the extrusion draw down and in the orientation zone are associated with these discontinuities. This, we have found, limits the fineness of the filaments of polyetheretherketone that can be produced to between 50 and 100 microns depending on the effectiveness of the filtration used. 20 25

In the production of thin films using a slot die instability of the melt curtain edge occurs at thicknesses of about 20 microns and below.

In European Patent Application No 83304022.3 there is described a process of producing a fibre-reinforced composition comprising passing a plurality of continuous filaments of, for example, glass or carbon, through a melt comprising a mixture of a thermoplastic polymer, such as an aromatic polyetheretherketone, and a plasticiser which is thermally stable at least up to the temperature of the melt and having volatility characteristics such that the plasticiser can be volatilised from the composition below the decomposition temperature of the thermoplastic polymer but has sufficiently low volatility at the temperature of the melt to plasticise the polymer and provide a melt of reduced viscosity compared with the melt viscosity of the polymer alone. 30 35

We have now found that the addition of substantial quantities of a plasticiser as used in the process described in European Patent Application No 83304022.3 to a polyetherketone and more particularly a polyetheretherketone before it is melt spun gives rise to a very much more regular extrusion for otherwise similar processing conditions. In addition work done by the extruder screw is reduced considerably and it is possible to reduce the extruder temperature. Consequently we have found using the modified process that filament diameters in the range 20 to 50 microns can be produced without frequent filament breaks. 40 45

According to the invention, therefore, we provide a process of melt spinning a mono- or multi-filament yarn or of extruding a film from an aromatic polyetherketone and more particularly an aromatic polyetheretherketone in which, prior to spinning or extruding, there is admixed with the polyetherketone polymer a substantial proportion of a plasticiser which is thermally stable at the temperature of the melt and provides a melt of reduced viscosity compared with the melt viscosity of the polymer alone such plasticiser having volatility characteristics such that though some of the plasticiser volatilises from the spun yarn or extruded film during the process, more than 1% by weight of the plasticiser remains in the spun yarn or extruded film. 45 50

It will be realised, therefore, that in the process all of the plasticiser is not removed the yarn or film and indeed, for certain applications, there are advantages to be gained from this. 50

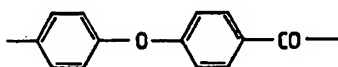
We also provide a melt spun mono- or multi-filament yarn or an extruded film of an aromatic polyetherketone and more particularly an aromatic polyetheretherketone containing in excess of 1% by weight of a plasticiser having the above defined stability and volatility characteristics. 55

Such a yarn or film can be readily converted into a porous yarn or film by an elevated heat treatment process between 250°C and 300°C preferably under vacuum. 55

According to another aspect of the invention, therefore, we provide a porous yarn or film of an aromatic polyetherketone and more particularly an aromatic polyetheretherketone.

By the term "substantial" which is used in connection with the proportion of plasticiser which is admixed with the polyetheretherketone polymer we mean that in the melt prior to spinning or extruding there is present in excess of 2% by weight of the plasticiser. 60

Suitable polyetherketones for use in the invention include those which contain the recurring unit (I):



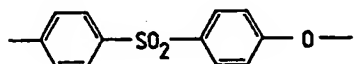
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Such polymers are disclosed, inter alia, in British patent specification 1 414 421 which describes such polymers containing the unit (I) as the sole repeating unit or in conjunction with the repeating unit (II):

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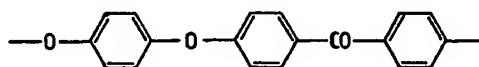
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A preferred polyetheretherketone having the repeating unit (III):



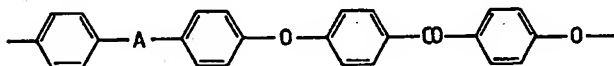
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either alone or in conjunction with other repeating units is disclosed in European patent publication No 1879. The other repeating units present in the polymers described in the European application may be of the repeating unit (IV):

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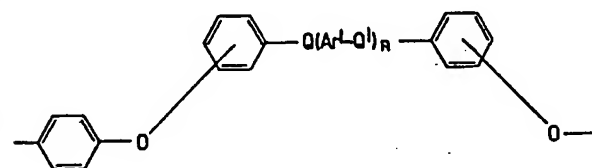
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where A is a direct link, oxygen, sulphur, $-\text{SO}_2-$, $-\text{CO}-$ or a divalent hydrocarbon radical. The repeat units may also be of formula (V):

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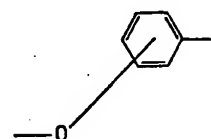
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where the oxygen atom in the sub-units:

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are *ortho* or *para* to the groups Q and Q', Q and Q' which may be the same or different are $-\text{CO}-$ or $-\text{SO}_2-$, Ar' is a divalent aromatic radical, and n is 0, 1, 2 or 3.

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The plasticisers which are suitable for use in the invention are materials which are thermally stable at the melt temperatures of polyetheretherketone and which can be partially volatilised from yarns or films during the production thereof in accordance with the invention process. Apart from that the plasticisers used will essentially have the capability of providing a plasticised polymer melt of lower melt viscosity than the polymer itself. Suitable plasticisers having these characteristics are found in the classes aromatic ketones, aromatic sulphones and aromatic esters. Typical plasticisers in these classes are diphenyl sulphone, ditolyl sulphone, benzophenone, phenyl benzoate and benzyl benzoate.

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The plasticiser and polymer may be admixed by any conventional technique. For example, a mixture may be achieved:— by dry blending the polymer and the plasticiser, by compounding in a screw extruder, by coating granules of the polymer with a solution of the plasticiser and volatilising the solvent from the coated granules or in suitable cases by adding the plasticiser in the course of producing the polymer.

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As mentioned above the mixture of the plasticiser and the polymer will have a reduced melt viscosity compared with the melt viscosity of the polymer alone. Furthermore we have found that the addition of the defined plasticiser serves to greatly reduce the tendency of the melt to

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